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Influence of Iron Bacteria on the Corrosion Behavior of Carbon Steel: SEM Study

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Graphical abstract

Abstract

In this work, the iron bacteria were cultured and inoculated into the cooling water before immersion, and low carbon steel coupons were immersed for one month. Then, microbially influenced corrosion (MIC) of carbon steel in the presence of these bacteria was investigated using scanning electron microscopy (SEM), x-ray diffraction spectroscopy (XRD) and weight loss methods. SEM results showed that large amounts of corrosion products and heterogeneous biofilm layer were formed on the coupon surface. SEM also revealed the uniform-pitting corrosion on the steel surface due to bacteria colonization. XRD results show that the main constituents present in corrosion product are composed of iron oxides and iron hydroxides.

Keywords: Microbially influenced corrosion, carbon steel, iron bacteria, SEM, XRD

Abstrak

Dalam penyelidikan ini, bakteria besi dibiakkan dan di inokulasi ke dalam air pendinginan sebelum rendaman, dan kupon keluli karbon rendah telah direndam selama satu bulan. Kemudian, kupon keluli karbon yang mengalami kakisan dipengaruhi mikrob (MIC) dengan kehadiran bakteria-bakteria tersebut dikaji dengan menggunakan kaedah misroskopi elektron imbasan (SEM), spektroskopi pembelauan sinar-x (XRD) dan kaedah kehilangan berat. Keputusan SEM menunjukkan terdapat jumlah yang besar produk kakisan dan lapisan biofilem heterogen terbentuk di atas permukaan kupon. Keputusan SEM juga menunjukkan kakisan bopeng seragam berlaku diatas permukaan keluli disebabkan penjajahan bakteria. Keputusan XRD menunjukkan juzuk utama terdapat didalam produk kakisan terdiri daripada oksida besi dan hidroksida besi.

Kata kunci: Kakisan dipengaruhi mikrob; keluli karbon; bakteria besi; SEM; XRD

1.0 INTRODUCTION

Microbially influenced corrosion or MIC is known as one of the destructive types of corrosion caused by activities of micro-organisms such as bacteria. The bacteria colonization and biofilm formation on the metal surface is recognized as the first stage of microbially influenced corrosion [1-3]. The appearance of metal surface due to MIC is mostly in the form of localized corrosion such as pit or crevice [4, 5]. Bridges, water cooling systems, ships and many types of equipments in an aquatic environment are some examples, which are in danger of failure due to MIC [6-9].

Carbon steel owes to its good mechanical properties, and low cost belongs to the most applicable metals in industry. However, the main limitation to use it in an aquatic environment is its less resistivity to corrosion. Carbon steel can corrode in bacteria inoculated environment such as a cooling water system as a result of bacteria colonization [10, 11]. One type of bacteria which could induce the corrosion process on the carbon steel is iron bacteria. This type of bacteria tends to oxidize the insoluble ferrous ions to soluble ferric ions, thereafter led to precipitation of Fe $(OH)_3$ on the steel surface. Thus, iron bacteria in the biofilm state could produce large amounts of corrosion products composed of iron oxide, and hydroxide precipitates on the steel surface [11, 12]. Due to the importance of iron bacteria in corrosion of metals, the present study is carried out to achieve a better understanding on MIC behavior of carbon steel in the presence of iron bacteria. In this work, SEM and XRD techniques were used to characterize the biofilm layer, corrosion products and study pitting corrosion on the steel surface.

■2.0 MATERIALS AND METHODS

2.1 Preparation of Coupons

Low carbon steel (99.6% of Fe, 0.028% of carbon, 0.030 of phosphorus, 0.035% of sulphur and 0.30% of copper.) coupons with a diameter of 20 mm and thickness of 4 mm were used as test material. The surfaces of the coupons were sequentially ground with a series of grit SiC papers (180, 500, 800, and 1200) and polished using 0.3 µm alumina powders. Coupons were rinsed with deionized water, followed by degreasing with acetone, and dried in at room temperature. The prepared coupons were then immersed in the bacteria inoculated medium.

2.2 Growth of Bacteria

Iron bacteria were cultured on the agar plate by serial dilution technique. In this method, eight small test tubes and agar plates were prepared. These tubes were filled up with water. In the first tube, 1 ml of the cooling water was diluted with 9 ml of distilled water. The mixture was shaken in the shaker for 24 hours with speed of 150 rpm at 30ºC temperature. From the first tube, 1 ml of the water dilution was transferred into the second tube contains 9 ml of distilled water. The second tube was also shaken in the shaker for 24 hours with speed of 150 rpm at 30ºC temperature. This similarly procedure was repeated for the 6 remaining tubes and spread plates. The optical density (OD) values were recorded for each tube. Finally, when the OD reached to the higher value, then 0.1 ml of the dilution from the considered tube was spread over the agar plate. Thereafter, the agar plate was incubated in the incubator oven at a temperature of 30 °C for 24 hours. Iron bacteria were transferred from the inoculated agar plate to the cooling water to assess the MIC behavior of carbon steel in the presence of bacteria. Total eight spread plates (with different dilution factor) were sealed with paraflim to prevent mixing up with other impurities present in the air. These bacteria were taken and inoculated in the cooling water before immersion of the steel coupons.

2.3 Immersion Test

The immersion test had been carried out by exposing the coupons in the bacteria inoculated medium for one month. For comparison purposes, the coupons were immersed in two types of cooling water in the presence of iron bacteria (biotic coupon) and (b) cooling water without the presence of iron bacteria (control coupon). At the end of immersion time the coupons were dried followed by mechanical and chemical cleaning in accordance to the ASTM standard (Designation: G1-03) for weight loss measurement.

2.4 SEM Analysis

Biofilm layer and corrosion products formed on coupons were analyzed by scanning electron microscopy. The dried samples were coated with a thin gold layer and observed under the field emission electron microscope. Furthermore, the pitting corrosion appeared on the steel surface is observed using scanning electron microscope.

2.5 XRD Characterization

An X-Ray Diffraction method was carried out to detect the chemical composition of the corrosion products formed on the steel surface due to bacterial colonization.

2.6 Corrosion Rate Measurement

Coupons were cleaned and weighed after drying. The weight loss was determined based on the difference between their initial and final weight of the coupon after an immersion test. The corrosion rate were calculated based on Equation (1).

$$\text{Corrosion rates} = (K \times W) / (A \times T \times D) \quad (1)$$

Where: $K = 2.40\times10^6$ D, T = time of exposure (hr), A = exposed surface area (cm^2), W = mass loss (g), D = density (g/cm^3)

■3.0 RESULTS AND DISCUSSION

3.1 Material Characterisation

The microstructure of carbon steel coupons observed by optical image analyser is shown in Figure 1. The microstructure is composed of ferrite phase (white region) and pearlite phase (dark region).

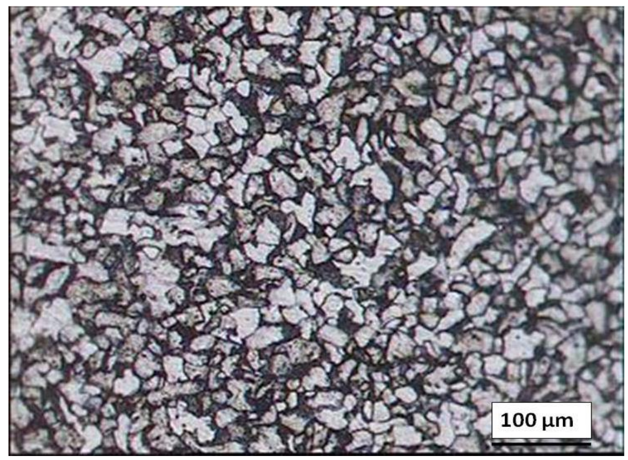

Figure 1 Optical micrograph of carbon steel (magnification ×100)

Generally, ferrite (α) is pure iron, and the pearlite is a fine mixture of ferrite and cementite (Fe_3C) in the lamellar form. In fact, the composition of the steel surface is an ideal surface for bacterial colonization and biofilm development. The bacteria nucleated and formed colonies on the coupon surface due to the presence of iron element that was required the bacterial growth.

3.2 Detection of Bacteria

In order to ensure that bacteria was present in the cooling system the presence of iron bacteria in water taken from the cooling system was identified using IRB BART kits. Figure 2(a) shows the control test tube containing filter sterilized cooling water. Figure 2(b) and (c) show the tubes contain the mixture of cooling water and iron bacteria.

Figure 2 IRB-BART Kits (a) Control set. (b) and (c) Bacterial samples

Figure 2(b) and (c) also showed that the color of water samples changed from yellowish to orange, which is due to the formation of ferric compounds by iron bacteria. Thus, the presence of iron bacteria in the cooling water system was confirmed.

3.3 Surface Analysis

Figure 3 shows the surface of as-received sample before immersion in the solution. The surface is clean without any trace of corrosion product.

Figure 3 As-received carbon steel coupon

Figure 4, however, shows the sample corroded after immersion in the bacteria-containing solution and in the control medium. It was found that the corrosion product is brownish in colour (Figure 4 (a) and (c)) which is typical colour of iron rust. When the corrosion products were removed, it appears that the coupon has lost some of its material, which is indicated by a rough surface.

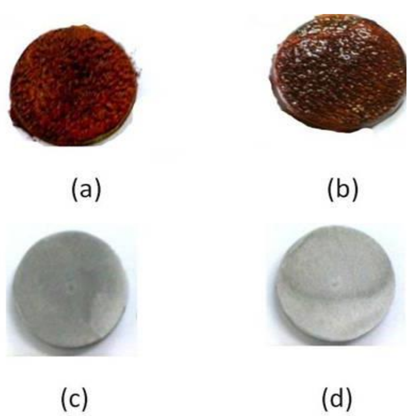

Figure 4 (a) Corroded biotic coupon (before cleaning) (b) Corroded control coupon (before cleaning) (c) Corroded biotic coupon (After cleaning) (d) Corroded control coupon (After cleaning) after 1 month exposure time

Based on visual inspection, the biotic coupon has more corrosion products compared with the control sample, and thus it can be deduced that the presence of bacteria has increased the corrosion rate of the coupon and the weight loss. Iron bacteria tend to oxidize insoluble ferrous ions to soluble ferric ions that lead to precipitation of Fe $(OH)_3$ on the steel surface.

The optical micrograph and SEM image of steel exposed to bacteria inoculated medium for one month is shown in Figure 5 and 6 respectively.

Figure 5 Optical micrograph (×570) of uniform pitting on the carbon steel coupon exposed to iron bacteria inoculated medium for one month

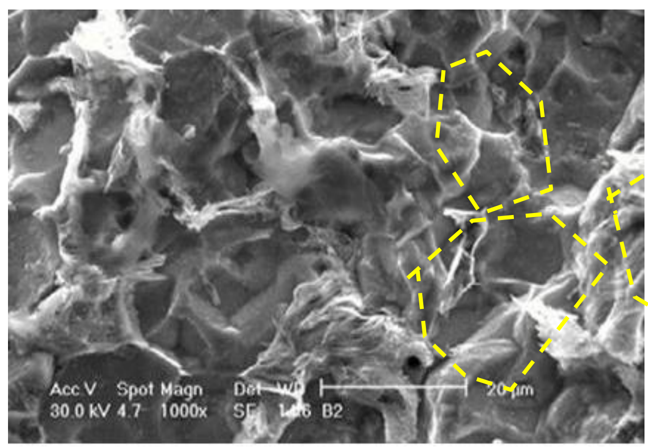

Figure 6 Scanning electron micrograph (SEM) of uniform pitting on the carbon steel surface exposed to iron bacteria inoculated medium for one month

The occurrence of uniform pitting corrosion on the steel surface is observed. In general, the appearance of steel due to MIC is accepted to be localized as it is under the influence of patchy biofilm that differential aeration cells and thus anodes and cathodes are formed. However, at some points on the steel surface, the pitted areas could be joint, thereby the appearance might look like a uniform pitting corrosion [10].

As seen in Figure 6, the occurrence of pitting corrosion on the carbon steel surface as a result of biofilm formation. In fact, under aerobic conditions, the biofilm formation usually leads to the creation of differential aeration cells. The generation of these cells is recognized to be destructive to the structure of the passive film and promote the pitting corrosion [13, 14]. Thus, the iron bacteria could facilitate the occurrence of pitting corrosion through biofilm formation and generation of brittle corrosion products.

Generally, it is impossible to make a relationship between the pit morphology and the type of bacteria. It has been found that the pit morphology could be formed by factors other than bacteria colonization. Furthermore, the pit morphology is more related to biofilm layer formed by bacteria not any specific bacterial types. Thus, the biofilm layer formed by different types of bacteria could result in formation of a pit of similar appearance [15, 16].

3.4 Biofilm and Corrosion Product Analysis

Figure 7 shows the SEM image of carbon steel exposed for one month in iron bacteria inoculated cooling water.

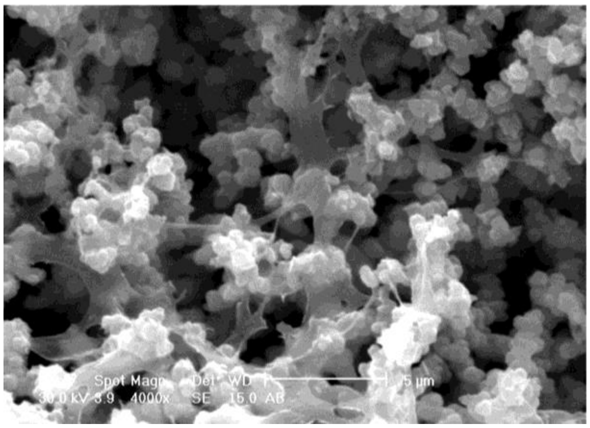

Figure 7 Scanning electron micrograph showing the hold fast structure by which the iron bacteria filaments attach to the metal surface and colonize

The whole surface of steel surface is covered with a heterogeneous biofilm layer and corrosion products. Biofilm layer is encrusted with corrosion products, which means that the formation rate of corrosion products is higher than the formation rate of biofilm layer. In view of the energetic involved large amounts of iron must be oxidized to supply the energy requirements for bacteria growth. Thus, the corrosion products are usually in larger amounts compared with bacterial biomass.
Figure 7 also shows the mode of attachment of iron bacteria filaments to the corrosion products; indicate that the oxide corrosion products are suitable places for growing of bacteria. Actually, the bacteria develop at the edge of the tubercle where oxygen and iron are readily available, since iron bacteria require oxygen for their growth [11].

Generally, as the first attachment of bacteria cells to the steel surface, they tend to form a biofilm layer to survive and prolong their lives. Biofilm secretes polymeric substances known as EPS to facilitate its growth. Extracellular polymeric substances are comprised of macromolecules such as proteins, polysaccharides, nucleic acids and lipids. EPS tend to attach to the corrosion products, to gain elements for bacterial growth. The activity and growth of bacteria could be increased through feeding from the corrosion products, which are enriched of oxygen [2, 17].

Figure 8 shows SEM images of some corrosion products formed on the carbon steel surface that was exposed to medium containing the iron bacteria for one month.

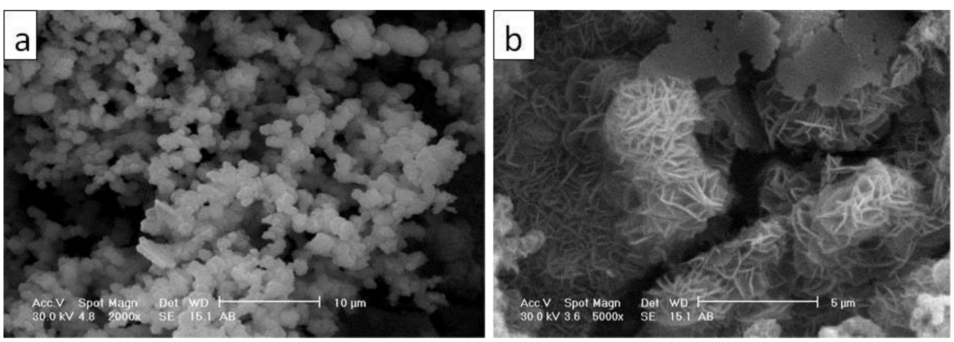

Figure 8 SEM micrographs showing: (a) fine plates (‘‘flowery’’ structures) typical of lepidocrocite, (b) globular (‘‘cotton balls’’) structures typical of goethite

The corrosion products are mainly iron oxides and hydroxides. The morphological structures of corrosion products are flowery structures of lepidocrocite and the typical cotton ball structure of goethite [14]. Normal corrosion products formed on carbon steel in aerobic condition are called tubercles. The formation of tubercles can be described as follows;

$$Fe \longrightarrow Fe^{+2} + 2e^- \quad \text{(anode)} \qquad (2)$$
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad \text{(cathode)} \qquad (3)$$
$$2Fe^{+2} + \tfrac{1}{2}O_2 + 5H_2O \longrightarrow 2Fe(OH)_3 + 4H^+ \quad \text{(tubercle)} \qquad (4)$$

Generally, iron can exist in three oxidation states (Fe^0, Fe^{2+} and Fe^{3+}). In presence of oxygen, the metallic iron (Fe^0) oxidises to form the stable Fe^{2+}. Subsequent oxidation of Fe^{2+} to Fe^{3+} takes place at pH >5 could produce energy for growth and activity of iron bacteria. Since the amount of energy extracted from this reaction is quite small for iron bacteria, (approximately −31 kJ), large quantities of Fe^{2+} have to be oxidized to Fe^{3+} to generate enough energy for bacteria growth and biofilm formation [18]. Thus, a large amount of corrosion products could be formed on the carbon steel due to presence of iron bacteria.

As shown in Figure 9, the XRD analysis was also carried out to confirm that the major constituents of the corrosion products in presence of iron bacteria are: goethite (α-FeOOH), wustite (FeO), magnetite (Fe_3O_4), hematite (Fe_2O_3) and Lepidocrocite (γ-FeOOH).

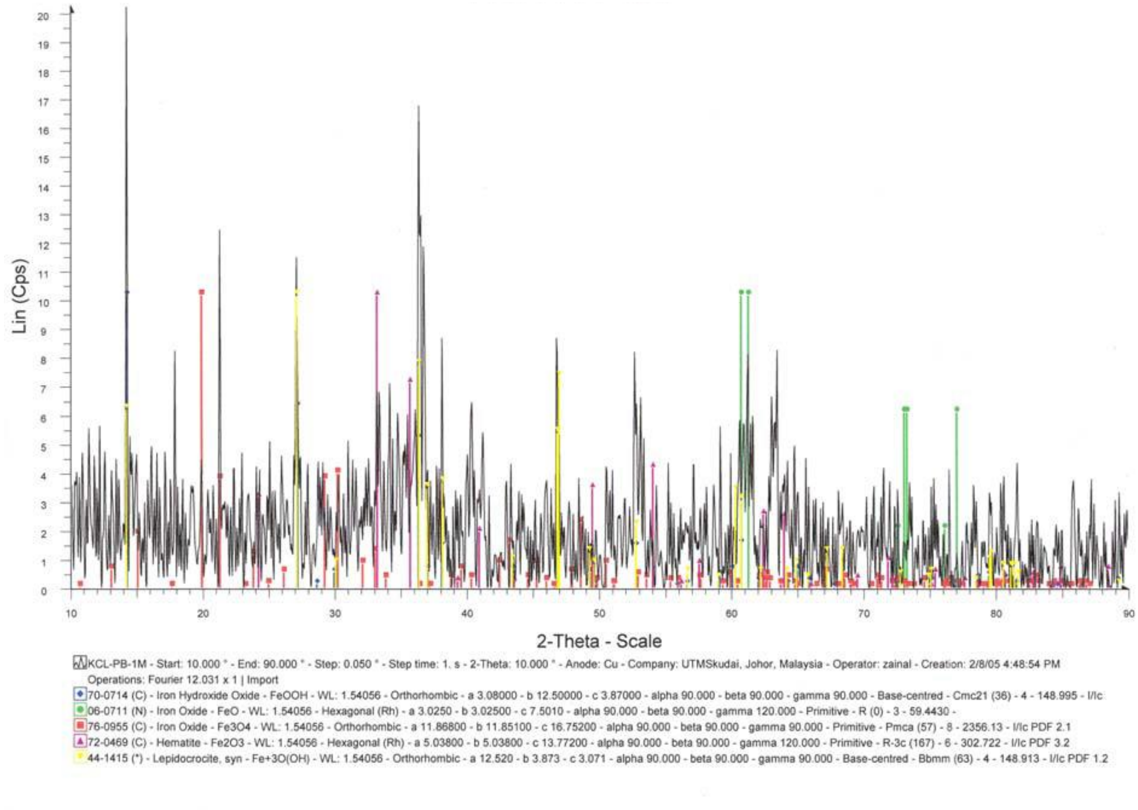

Figure 9 X-Ray Diffraction analysis of corrosion products in presence of iron bacteria

3.5 Corrosion Rate Measurement

The corrosion rate of the biotic and control coupons was determined based on Equation (1) using the weight loss method to evaluate the corrosion damage on the coupons in one month.

Figure 10 shows the corrosion rate of biotic and control coupons.

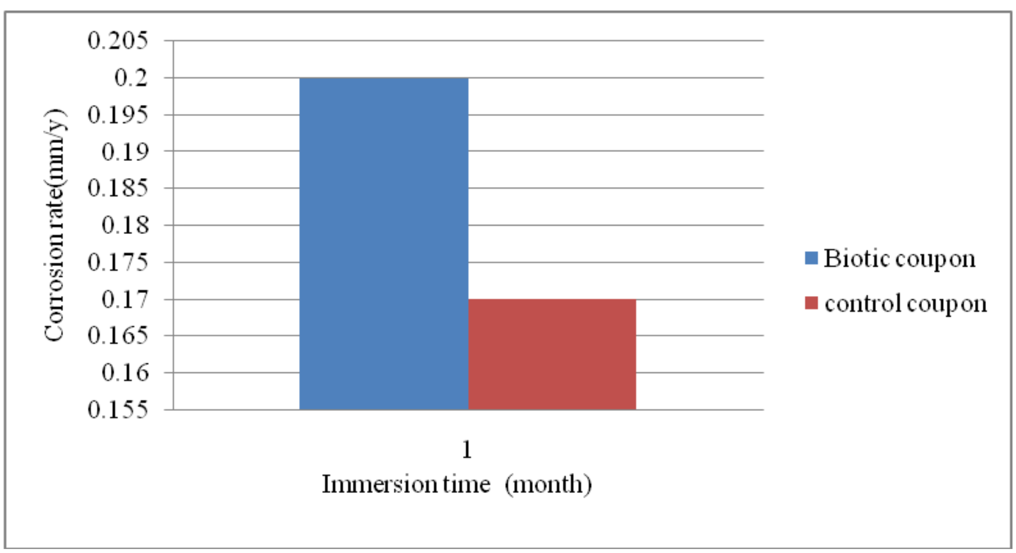

Figure 10 Corrosion rates of the biotic and control coupons in one month immersion time

Figure 10 shows that the corrosion rate of biotic coupons is higher than the corrosion rate of control coupons. Thus, it be concluded that iron bacteria accelerate the corrosion rate of biotic coupons. Large amounts of iron must be oxidized to supply the energy requirements for growth of iron bacteria. This phenomenon accelerates the corrosion rate of biotic coupons. However differential aeration cell could also accelerate the corrosion rate of biotic coupons. In differential aeration cell, the area beneath the biofilm is lacked of an oxygen act as an anode and the metal surface which is enriched of the oxygen act as a cathode. Thus, the corrosion process on the surface of biotic coupons was enhanced [18, 19].

4.0 CONCLUSION

1. Carbon steel immersed in solution contains iron bacteria (biotic coupon) has more corrosion product carbon steel immersed in solution without presence of iron bacteria (control coupon). Thus, iron bacteria are responsible for accelerating the corrosion rate and formation of more corrosion products on the biotic coupon surface.
2. The corrosion process on the carbon steel surface was affected by the presence of iron bacteria. The bacteria in the form of biofilm lead to the formation of differential aeration and concentration cells, causing uniform pitting corrosion on the steel surface.
3. SEM results showed large amounts of corrosion products, and heterogeneous biofilm layer formed on the coupon surface in presence of iron bacteria.
4. XRD analysis showed that major constitute of corrosion products are: iron oxide hydroxide goethite (α-FeOOH), wustite (FeO), magnetite (Fe_3O_4), hematite (Fe_2O_3) and Lepidocrocite (γ-FeOOH).

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